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This document reports on work performed under the grant FA9550-04-1-0057, Air Force Office of Scientific Research, $474,927, Feb 15, 2004 - Dec 31, 2006. During this period, we have extended our preliminary investigations of azide photochemistry, with the aim of demonstrating unambiguously the photochemical production of cyclic-N, and of revealing the fundamental photochemical mechanism of N-N-N ring closure in azide photochemistry. The remainder of this report is organized as follows. First, we present a list of publications and scientific presentations of the work supported by this grant. A brief review of the important results is then presented.

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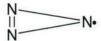| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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Final Technical Report
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Overview

This document reports on work performed under the grant: *FA9550-04-1-0057, Air Force Office of Scientific Research, $474,927, Feb 15, 2004 - Dec. 31, 2006.* During this period, we have extended our preliminary investigations of azide photochemistry, with the aim of demonstrating unambiguously the photochemical production of cyclic-N_3,

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and of revealing the fundamental photochemical mechanism of N-N-N ring closure in azide photochemistry. The remainder of this report is organized as follows. First, we present a list of publications and scientific presentations of the work supported by this grant. A brief review of the important results is then presented.

Publications Resulting From This Work

1. *Interaction of NO(v=12) with LiF(001): Anomalously large vibrational relaxation rates,* Alec M. Wodtke and Yuhui Huang, Daniel J. Auerbach, <u>Journal of Chemical Physics</u> **118**(17) 8033-41 (2003)

2. *Ion Dissociation Dynamics of the Chlorine Azide Cation (ClN₃⁺) Investigated by Velocity Map Imaging*, N. Hansen, A. V. Komissarov, K. Morokuma, M. C. Heaven and A. M. Wodtke, Journal of Chemical Physics **118** 10485-10493 (2003)

3. *Transport and focusing of highly vibrationally excited NO molecules,* Daniel Matsiev, Jun Chen, M. Murphy, A.M. Wodtke Journal of Chemical Physics **118** 9477-9480 (2003)

4. *Velocity map ion imaging of ClN₃ photolysis: Evidence of photolytic production of cyclic-N₃.* N. Hansen and A. M. Wodtke, Journal of Physical Chemistry (Charles Parmenter Festschrift) **107**(49), 10608-10614 (2003).

5. *Hexapole focusing of vibrationally excited molecules prepared by optical pumping,* Jun Chen, Jason White, Daniel Matsiev, Michael Murphy, Alec M. Wodtke, Chem. Phys. **301**(2-3) 161-172 (2004)

6. *The Cl to NCl branching ratio in 248-nm photolysis of chlorine azide,* Alec M. Wodtke, Nils Hansen, Niels Sveum, Jason Robinson, Scott Goncher and Daniel M. Neumark, Chem. Phys. Lett. **391** 334-337 (2004).

7. *Invited Review in the International Reviews of Physical Chemistry.* "Electronically non-adiabatic interactions of molecules at metal surfaces: Can we trust the Born-Oppenheimer approximation for surface chemistry?" Alec M. Wodtke, John C. Tully, Daniel J. Auerbach, International Reviews in Physical Chemistry, **23**(4), 513-539 (2004).

8. Invited Chapter for Advanced Series in Physical Chemistry, World Scientific, Chuik Ng Series Editor, "Modern Trends in Chemical Reaction Dynamics Part II: Experiment and Theory". *Ed.'s Xueming Yang and Kopin Liu,* "Interactions of vibrationally excited molecules at surfaces: A probe for electronically non-adiabatic effects" Alec M. Wodtke, vol. **14**, 383-408 (2005).

9. *High Level ab initio studies of unimolecular dissociation of ground state N₃ radical,* Peng Zhang, Keiji Morokuma, Alec M. Wodtke, J. Chem. Phys. **122**, 014106-1-11 (2005)

10. *Two photoionization thresholds of N₃ produced by ClN₃ photodissociation at 248 nm: Further evidence for cyclic N₃,* Petros Samartzis, Jim Jr-Min Lin, Tao-Tsung Ching, Chanchal Chadhuri, Yuan T. Lee and Alec M. Wodtke, J. Chem. Phys., **123**, 051101 (2005)

11. *Photofragment Translational Spectroscopy of ClN₃ at 248 nm: Determination of the Primary and Secondary Dissociation Pathways.* N. Hansen, A.M. Wodtke, S. J. Goncher,

J. Robinson, N. Sveum, D. M. Neumark, J. Chem. Phys., **123** (10): Art. No. 104305 (2005)

12. An experimental and theoretical study of ring closing dynamics in HN_3, Jianyang Zhang, Yuan Chen, Kaijun Yuan, Steven A. Harich , Xiuyan Wang, Xueming Yang, Peng Zhang, Zhi Wang, Keiji Morokuma and Alec M. Wodtke Physical Chemistry Chemical Physics, **8**, 1690 – 1696 (2006)

13. *Imaging ClN_3 photodissociation from 234 to 280 nm* Peter C. Samartzis, Nils Hansen, and Alec M. Wodtke, Phys. Chem. Chem. Phys., **8**, 2958 – 2963 (2006)

14. *The heat of formation of chlorine-isocyanate and the relative stability of isoelectronic molecules: an experimental and theoretical study.* Yuanyuan Ji, Petia Bobadova-Parvanova, Chris Larson, Petros Samartzis, Keiji Morokuma, Jim Jr-Min Lin, Tao-Tsung Ching, Chanchal Chadhuri, Shih-Huang Lee and Alec M. Wodtke, J. Chem. Phys. **124**(24), Art. No. 241106 (2006)

15. *Collision-free photochemistry of methylazide: Observation of unimolecular decomposition of singlet methylnitrene,* Christopher Larson, Yuanyuan Ji, Petros Samartzis, Alec M. Wodtke, Shih-Huang Lee, Jim Jr-Min Lin, Chanchal Chaudhuri, and Tao-Tsung Ching J. Chem. Phys. **125**, 133302 (2006)

16. *All-nitrogen chemistry: How far are we from N_{60} ?* Petros C. Samartzis and Alec M. Wodtke, International Reviews in Physical Chemistry, **25** (4): 527-552 (2006).

17. *The Simplest all-Nitrogen Ring: Photolytically filling the cyclic-N_3 well* Petros Samartzis, Jim Jr-Min Lin, Tao-Tsung Ching, Chanchal Chaudhuri, Shih-Huang Lee and Alec M. Wodtke J. Chem. Phys. **126** (4) Art. No. 041101 (2007)

Accepted or in press

18. *Casting a new light on azide photochemistry: Photolytic production of cyclic-N_3.* Peter C. Samartzis, and Alec M. Wodtke, Invited Review Article for Physical Chemistry Chemical Physics. (in press)

19. *Dissociative photoionization of ClN_3 using high-resolution synchrotron radiation: The N-Cl bond energy in ClN_3,* Alfredo Quinto, Yin-Yu Lee, Tzu-Ping Huang, Wan-Chen Pan, Jim Jr-Min Lin, Petia Bobadova-Parvanova, Keiji Morokuma, Petros Samartzis, and Alec M. Wodtke (accepted in International Journal of Mass Spectrometry special issue to honor Dr. Jean H. Futrell.)

In preparation

20. *Observation of photochemical C-N bond cleavage in CH_3N_3, a new photochemical route to cyclic-N_3*, Chris Larson, Yuanyuan Ji, Peter C. Samartzis, Jim Jr-Min Lin, Tao-Tsung Ching, Chanchal Chaudhuri, Alec M. Wodtke, in preparation for J. Chem. Phys.

Scientific Presentations of the Work Supported by This Grant

1. Invited Lecture, Physical Chemistry Seminar, Evidence for Photolytic Production of Cyclic-N_3, Marquette University, Dec. 17 2004.

2. Poster Presentation, Gordon Conference on Molecular Energy Transfer, Jan 9-14 2005 Buellton CA, "Photofragment Translational Spectroscopy of ClN_3: Cl to NCl Branching Ratio and Bimodal Translation Energy Distribution in the Radical Channel"

3. Poster Presentation, Gordon Conference on Molecular Energy Transfer, Jan 9-14 2005 Buellton CA, "ClN_3 photodissociation at 248 nm , studied by synchrotron ionization of photofragments"

4. Poster Presentation, Gordon Conference on Molecular Energy Transfer, Jan 9-14 2005 Buellton CA, "Hexapole focusing of vibrationally excited molecules prepared by optical pumping"

5. Invited Lecture, "Evidence for Photolytic Production of cyclic-N_3", Dalian Institute of Chemical Physics, Dalian China, March 18 2005

6. Invited Lecture, "Evidence for Photolytic Production of cyclic-N_3", Institute for Chemistry, Beijing, China, March 21 2005

7. Invited Lecture, "Evidence for Photolytic Production of cyclic-N_3", University of Science and Technology, Hefei China, March 22, 2005

8. Invited Lecture, Pacifichem, Honolulu, HI, Evidence for Photolytic Production of Cyclic-N_3, Dec. 9-14, Dec. 15-20 2005

9. Invited Lecture, Photochemical Production of Cyclic-N_3, Airforce Office of Scientific Research Contractors Meeting, Arlington VA, June 5-7, 2006.

10. Invited Lecture, "Photochemical Production of the Ring-closed form of N_3", Symposium on "Chemistry in Extreme Environments", American Chemical Society National

Meeting, Sept 10-14, 2006, San Francisco CA.

11. Invited Lecture, "Photochemical Production of the Ring-closed form of N_3", Polynitrogen Workshop, 15, 16 Sep 2006, University of Southern California, Los Angeles California

12. Invited Lecture, "Photochemical production of cyclic-N_3" 2007 Meeting of the Western Spectroscopy Association, Jan. 31-Feb 2 2007, Asilomar, California

13. Invited Lecture, "Photochemical production of cyclic-N_3", 29th International Symposium on Free Radicals, August 12-17, 2007, Big Sky Montana

Major results of the project

- The velocity map imaging technique was applied to study the unimolecular dissociation dynamics of the chlorine azide cation (ClN_3^+) fragmenting into N_2 and NCl^+ and the results were compared to quantum chemical calculations. The ClN_3^+ ion was produced in a molecular beam by two-photon ionization of chlorine azide (ClN_3) with laser light at $\lambda \approx 202$ nm. Rotationally resolved REMPI spectra and velocity map images of state selected N_2 ($X\,^1\Sigma_g^+$, v, J) quantify the energy deposition into N_2 and NCl^+ products. Photoelectron velocity map images show near zero-energy electron production. The N_2 ($X\,^1\Sigma_g^+$) dissociation products are mainly in the vibrational ground state, but rotationally excited with J up to ~60. An unusual vibrational distribution in the NCl^+ ($X\,^2\Pi$, $v = 1 - 12$) product was observed, which is evidence of non-statistical ion decomposition. This work also provides an accurate determination of the energetics for the reaction: $ClN_3^+ \rightarrow N_2$ ($X\,^1\Sigma_g^+$) + NCl^+ ($X\,^2\Pi$) ($\Delta E < -0.2$ eV), from which one may use prior photo-ionization threshold data to derive the energetics of the $ClN_3 \rightarrow N_2$ ($X\,^1\Sigma_g^+$) + NCl ($a\,^1\Delta$) ($\Delta E < 0.3$ eV) dissociation.

- The method of velocity map imaging was applied to study the photodissociation dynamics of ClN_3 near 235 nm under collision free conditions. Derived kinetic energy distributions of state-selected Cl (^2P_J) provide a medium resolution energy spectrum of the N_3 fragment. Markedly bimodal distributions are observed that suggest simultaneous formation of the linear N_3 ($\tilde{X}\,^2\Pi$) isomer as well as an energetic form of N_3 consistent with theoretical predictions of a cyclic isomer, exhibiting $^2B_1$ symmetry in the C_{2v} point

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group. Angular distributions of the photofragments indicate that $2^1A' \leftarrow 1^1A'$ excitation is the most important pathway to photoproducts. Branching ratio measurements between the dominant spin-orbit excited state Cl* $(^2P_{1/2})$ and the spin-orbit ground state Cl $(^2P_{3/2})$ showed Cl*/Cl $\approx 0.8/0.2$. The branching ratio between N$_3$ ($\tilde{X}\ ^2\Pi$) and N$_3$ ($^2B_1$) formation was determined to $\approx 0.8/0.2$.

- The primary reaction products from 248-nm chlorine azide photolysis were identified in a collision free experiment. In contrast to all previous reports, the radical channel producing Cl + N$_3$ (95 $\pm$ 3 %) is seen to dominate the photochemistry. The molecular channel producing NCl + N$_2$ (5 $\pm$ 3 %) was also observed.

- Photofragmentation translational spectroscopy was used to identify the primary and secondary reaction pathways in the KrF laser (248 nm) photodissociation of Chlorine Azide (ClN$_3$) under collision-free conditions. Both the molecular channel producing NCl $(X^3\Sigma, a\ ^1\Delta)$ + N$_2$ and the radical channel producing Cl (^2P_J) + N$_3$ were analyzed in detail. Consistent with previous reported velocity map ion imaging experiments [N. Hansen, A. M. Wodtke, *J. Phys. Chem. A*, **107**, 10608, (2003)] a bimodal translational energy distribution is seen when Cl atoms are monitored at m/z = 35 (Cl$^+$). Momentum-matched N$_3$ counter-fragments can be seen at m/z = 42 (N$_3^+$). The characteristics of the observed radical-channel data reflect formation of linear azide radical and another *high-energy form* of N$_3$ (*HEF-N$_3$*) that exhibits many of the characteristics one would expect from cyclic-N$_3$. *HEF*-N$_3$ can be directly detected by electron impact ionization more than 100 μs after its formation. Products of the unimolecular dissociation of *HEF*-N$_3$ are observed in the m/z = 14 (N$^+$) and m/z = 28 (N$_2^+$) data. Anisotropy parameters were determined for the primary channels to be: $\beta = -0.3$ for the NCl forming channel and $\beta = 1.7$ and $\beta = 0.4$ for the linear-N$_3$ and *HEF*-N$_3$ forming channels, respectively. There is additional evidence for secondary photodissociation of N$_3$ and of NCl.

- A comprehensive study of the unimolecular dissociation of the N$_3$ radical on the ground doublet and excited quartet potential energy surfaces was also carried out with multi-reference single and double excitation configuration interaction (MRCISD) and second order multi-reference perturbation (CASPT2) methods. Two forms of the N$_3$ radical were located in the linear and cyclic region of the lowest doublet potential energy surface

with an isomerization barrier of 62.2 kcal/mol above the linear N_3. Three equivalent C_{2v} minima of cyclic N_3 are connected by low barrier, meaning the molecule is free to undergo pseudo-rotation. The cyclic N_3 is metastable with respect to ground state products, $N(^4S) + N_2$, and dissociation must occur via intersystem crossing to a quartet potential energy surface. Minima on the seams of crossing between the doublet and quartet potential surfaces are found to lie substantially higher in energy than the cyclic N_3 minima. This strongly suggests that cyclic N_3 possesses a long collision free lifetime even if formed with substantial internal excitation.

- We carried out near-threshold photoionization of N_3 photofragments produced by laser photodissociation of ClN_3 at 248 nm. Time-of-flight (TOF) of recoiling N_3 is used to resolve two photochemical channels producing N_3, which exhibit different translational energy release. The two forms of N_3 resolved in this way exhibit different photoionization thresholds, consistent with their assignment to linear $(X\ ^2\Pi_g)$ and cyclic N_3. This result agrees with existing theoretical calculations of excited and ionic states of N_3 and strengthens previous experimental results which suggested the ClN_3 photolysis produces a cyclic form of N_3.

- We reported results of H(D)-atom Rydberg tagging experiment for $H(D)N_3$ photolysis providing detailed dynamical information on the wavelength dependence of the $H(D)+N_3$ channel. We observe subtle yet striking changes in the photochemical dynamics as the photolysis energy passes through ~5.6 eV. In addition to producing linear azide with an average of ~40% of available energy appearing as translation, a second H(D)-atom producing channel grows in above this energy releasing only about 15%. An observed (inverse) isotope effect suggests that statistical decomposition on S_0 is unimportant. High level *ab initio* quantum chemical calculations reveal a transition state to cyclization of the N_3 moiety in $H(D)N_3$ on the first excited singlet (S_1) surface that is close in energy to the experimentally observed threshold energy for this "slow channel". Furthermore, the translational energy release of the "slow channel" is energetically consistent with cyclic-N_3 formation. This work provides the clearest presently available insights into how ring closure can occur in azide photochemistry.

- We also reported $Cl(^2P_{3/2})$ and $Cl^*(^2P_{1/2})$ fragment images following ClN_3 photolysis in the 234-280 nm region measured by Velocity Map Imaging. Kinetic energy distributions change shape with photolysis wavelength from bimodal at 234 and 240 nm to single peak at 266 and 280 nm. Where two peaks exist, their ratio is significantly different for Cl and Cl* fragments. The single peak of 266 and 280 nm and the faster peak at 234 and 240 nm are assigned to a Cl + linear-N_3 dissociation channel, in agreement with previous work. The slow peak in the bimodal distributions is assigned to the formation of a high energy form (HEF) of N_3. Candidates for the identity of HEF-N_3 are discussed. Combining our data with photofragmentation translational spectroscopy results we determined the threshold for the appearance of HEF-N_3 at 4.83±0.17eV photolysis energy. This threshold behavior is similar to results on the wavelength dependence of HN_3 photolysis, where the threshold was associated with a ring closed isomer of HN_3 on the S_1 potential energy surface. We also note that the threshold HEF-N_3 formation threshold observed for ClN_3 occurs where the energy available to the products equals the isomerization barrier from linear to cyclic-N_3.

- We reported evidence that *cyclic-N_3* is exclusively produced in the 157-nm photolysis of ClN_3. Photoproduct translational energy measurements reveal a single-peaked distribution for an N_3-formation channel with maximum and minimum translational energies matching the theoretically predicted minimum and maximum binding energies of *cyclic-N_3*, respectively. The absence of linear-N_3 greatly simplifies the data analysis. The zero-Kelvin heat of formation of *cyclic-N_3* is derived experimentally (**142 ± 3.5 kcal/mol**) and is in excellent agreement with the best existing determinations from other studies.

- Accurate thermochemical data of small molecules are invaluable to the progress of every aspect of chemistry, especially in the atmosphere, combustion and industry. In this work, photofragmentation translational spectroscopy and 1st principles electronic structure theory reveal the literature value of the heat of formation of chlorine-isocyanate to be in error by more than 40 kcal/mol. We reported a revised experimental value for $D_0(Cl-NCO)=51 \pm 3$ kcal/mol which leads to a $\Delta H_f(ClNCO) = 8.5 \pm 3$ kcal/mol. High level ab initio (CCSD(T)) electronic structure calculations extrapolated to the complete basis set limit give $D_0(Cl-NCO) = 56.3$ kcal/mol, in good agreement with experiment. In light of the present results, the destabilization of azides relative to isoelectronic

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isocyanates has been evaluated empirically for three pairs of related molecules. It is found to be 90-110 kcal/mol, and has been attributed mainly to the weakening of the N-NN bond relative to the N-CO bond. Electronic structure calculations employing decomposition analysis suggest that, compared to homopolar N_2, the $^{+\delta}CO^{-\delta}$ σ polarity provides better orbital interaction (charge transfer) and electrostatic attraction and results in a closer encounter and larger stabilization between the fragments and that this is the origin of isoelectronic destabilization of azides relative to the isocyanates.

- Methylazide photolysis at 248 nm was also investigated by ionizing photofragments with synchrotron radiation in a photofragmentation translational spectroscopy study. CH_3N and N_2 were the only observed primary products. The translational energy release suggests a simple bond rupture mechanism forming singlet methylnitrene, $^1CH_3N$, and N_2. Thus, these experiments reveal the unimolecular decomposition of this highly unstable species. We explain our observations through a mechanism which is initiated by the isomerization of $^1CH_3N$ to a highly internally excited methanimine $H_2C=NH$ isomer, which decomposes by 1,1-H_2 elimination forming HNC + H_2 as well as sequential H-atom loss (N-H followed by C-H bond cleavage), to form HCN. No evidence for dynamics on the triplet manifold of surfaces is found.

- High resolution synchrotron-radiation-based photoionization mass spectrometry was applied to study the dissociative photoionization of ClN_3 under collision-free molecular beam conditions at ionization energies between 10 and 17 eV. No parent ion (ClN_3^+) could be detected under our experimental conditions. This suggests that the ground and excited states of ClN_3^+ are weakly bound or repulsive, a conclusion supported by electronic structure calculations also reported here. We recorded photoionization yield spectra at m/z=49, 42, 35 and 14 from which we extracted the appearance potentials for NCl^+, N_3^+, Cl^+, and N^+. The appearance potential of NCl^+ (10.17 ± 0.02eV) observed here is close to the previously reported ionization potential of ClN_3 obtained form photoelectron spectroscopy. Using the theoretically calculated binding energy of ClN_3^+ (0.2 eV), we derive an estimate of the *adiabatic* ionization potential of ClN_3 = 9.97 eV. The measured appearance potentials for N_3^+, Cl^+, and N^+ provide three independent determinations of the Cl-N bond energy in ClN_3, which agree within their respective error limits. The observations of this work are consistent with a new value of the N-Cl bond energy in ClN_3, $D_0(Cl-N_3)$=1.86 ± 0.05 eV, 0.3 eV lower than previously reported values,

which are however experimentally derived upper limits. The bond energy reported here is consistent with high level *ab initio* (CCSD(T)) electronic structure calculations extrapolated to the complete basis set limit, which yield a value: $D_0(Cl-N_3)=1.87$ eV.

- In work that is yet to be published we observe the production of methyl and N_3-radical in the collision-free, 193-nm photodissociation of methylazide and record the translational energy release of this reaction. The most probable translation energy release is only 8% and the maximum observed translational energy release is only 60% of the available energy assuming linear-N_3 formation. The maximum translational energy release is quantitatively consistent with production of cyclic-N_3. Threshold photoionization of the N_3 fragment also shows results consistent with theoretical prediction of the cyclic-N_3 ionization potential. The secondary dissociation of $N_3 \rightarrow N(^2D) + N_2$ is also observed and its translational energy release is derived. This distribution peaks at 5 and extends to about 10 kcal/mole as would be expected from the size of the exit channel barrier for spin-allowed dissociation of cyclic N_3 (7 kcal/mol) and, furthermore, inconsistent with the barrier height of the spin allowed dissociation of linear N_3 (3 kcal/mol). A large fraction (1/2) of the N_3 does not dissociate on the microsecond time scale meaning methylazide may be the most attractive photochemical precursor of cyclic-N_3 yet found.